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Abstract

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The metallurgy and electrical performance of contacts to GaN were examined. Thermodynamic estimates coupled with experimental work revealed clear trends in the nature of the contact metallurgy depending upon the position of the metal in the periodic table. This information was then used to aid in the investigation and design of electrical contacts to GaN. Ohmic contacts to n-GaN, Schottky barriers to n-GaN, and ohmic contacts to p-GaN were fabricated and characterized. These studies resulted in an improved understanding of the mechanism of ohmic contact formation in Al/Ti/n-GaN contacts, along with the development of TiN/Ti/n-GaN and ZrN/Zr/n-GaN ohmic contacts with exceptional thermal stability at 600 °C and contact resistivities of 6×10^{-6} and 2×10^{-5} $\Omega \cdot cm^2$, respectively, for $n = 7 \times 10^{17}$ cm^{-3}. Also developed were Re/n-GaN Schottky barrier contacts that were stable upon annealing at 700 °C with current-voltage and capacitance-voltage barrier heights of 0.82 and 1.06 eV, respectively. For ohmic contacts to p-GaN, a large number of contacts were evaluated. A clear improvement over conventional Au/Ni/p-GaN contacts was provided by electrodeposited Pt/p-GaN and sputtered Pt/Ni/p-GaN contacts, which provided contact resistivities that were lower than Au/Ni/p-GaN contacts by more than a factor of two. An explanation for this improvement was formulated.

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1. Introduction

Along with rapid advancement in the development of III-V nitride materials and devices has come the need for high performance electrical contacts to these semiconductors. This document contains the major findings of a study of the metallurgy and electrical performance of contacts to GaN performed at The Pennsylvania State University during the period September, 1995–September, 1998. The findings of this study are discussed in four sections, which cover metallurgical considerations, ohmic contacts to n-GaN, Schottky barriers to n-GaN, and ohmic contacts to p-GaN.

2. Metallurgical Considerations

2.1 Thermodynamic Predictions

Early in this project, phase equilibria in the metal-Ga-N systems were predicted based on thermodynamic considerations [1]. This information was expected to be useful both for predicting the nature of the reaction between the metal contacts and GaN and for selecting thermally stable contact materials. Our original predictions are summarized in Fig. 1. Some metals are not shaded in the figure because inadequate thermodynamic data were available for those systems. However, these metal-Ga-N systems can be expected to exhibit similar features to those nearby in the periodic table because of systematic trends in the thermodynamic stability of metal gallides and nitrides across the periodic table.

The stability of the early transition metal nitrides dominates the metallurgy of the early transition metal-Ga-N systems. Thermodynamic calculations indicate that none of these metals are in thermodynamic equilibrium with GaN under conditions of interest for processing contacts to GaN, and interfacial reactions are favored to take place in the metal/GaN contacts upon annealing at temperatures high enough to permit interdiffusion. The mononitrides of the early transition metals are particularly stable. Some of these nitrides, such as TiN and ZrN, are refractory, exhibit metallic conductivity [2], and possess work functions below 4 eV [3], which make them attractive for use in thermally stable ohmic contacts to n-GaN. Interaction with the annealing environment was also predicted

for the early transition metals, which could be nitrided when annealed in N_2 gas if the kinetics of such a reaction permit.

It was predicted that some of the middle transition metals (Re and W) could be thermally stable single metal contacts to GaN at 600 °C. In contrast, late transition metals, particularly Ni, Pd, and Pt, were expected to react with GaN at elevated temperatures to form metal gallides and release N_2 gas, even when annealed at 600 °C under 1 atm of N_2.

2.2 Experimental Findings

Recently, we compared these predictions to experimental findings, both our own and those from other groups. The experimental findings are summarized in Fig. 1. The early transition metal nitrides Ti, V, and Cr are indeed dominated by the stability of the metal nitrides, as can be seen in Fig. 2, which shows portions of isothermal sections of these phase diagrams experimentally determined by us [4, 5] for a temperature of 800 °C. These diagrams indicate that the only solid phases in thermodynamic equilibrium with GaN under conditions of interest for processing metal/semiconductor contacts are the metal mononitrides. Our findings on the stability of ZrN-based contacts to n-GaN [6] indicate a similar situation for Zr.

Because titanium is the early transition metal that has been used most frequently in ohmic contacts to n-GaN, we will focus in more detail on this metal, choosing it to illustrate features expected to be common to the early transition metals. The formation of TiN in Ti/n-GaN contacts has been observed both by us [7] and others [8] and is not surprising. Titanium is not in thermodynamic equilibrium with GaN, and it is possible from the phase diagram to identify the equilibrium reaction products when Ti/GaN contacts are annealed in a closed system—one in which no material is lost or gained through interaction with the environment. Since the only condensed (solid or liquid) phases in thermodynamic equilibrium with GaN are TiN and Ga, Ti will react with excess GaN in a closed system to form TiN and liquid Ga on the remaining GaN layer, consistent with the overall composition of the sample.

The nature of this reaction, however, does depend upon the environment in which the contacts are annealed. When contacts are annealed in an open system (one in which elements may be exchanged with the environment), the result can be quite different. The partial Ti-Ga-N phase diagram of Fig. 2 represents only the condensed phase equilibria. Consider the tie-triangle representing the thermodynamic equilibrium between GaN, TiN, and liquid Ga. The activity of each element is fixed within this (or any) three phase region, and as a result, there is only one N_2 partial pressure at a given temperature under which these three phases are simultaneously in equilibrium. The equilibrium N_2 pressure over GaN and liquid Ga (and hence over GaN, liquid Ga, and TiN at the composition at which they are all three in equilibrium) can be estimated using the following equation

$$p_{N_2} = \frac{a_{GaN}}{a_{Ga}} p^{o}_{N_2} \exp\left\{-\frac{2\Delta S^{o}_{f}}{R}\right\} \exp\left\{\frac{2\Delta H^{o}_{f}}{RT}\right\},$$

where a_{GaN} is the activity of GaN (equal to 1), a_{Ga} is the activity of liquid Ga (approximately 1 since there is limited solubility of N and Ti in liquid Ga at temperatures of interest), $p^{o}_{N_2}$ is the standard state pressure of 1 atm, ΔS^{o}_{f} is the standard entropy of formation of GaN, ΔH^{o}_{f} is the standard enthalpy of formation of GaN, R is the gas constant, and T is the absolute temperature. In this estimate, the standard enthalpy of formation (-158 kJ/mol) and entropy of formation (-135.7 J/mol K) reported by Karpinski and Porowski [9] have been used. (These values have been reported to be nearly constant with temperature.) At 700 °C, an equilibrium nitrogen partial pressure of 0.006 atm over coexisting GaN, TiN, and liquid Ga can be estimated. What happens if the contacts are instead annealed in 1 atm N_2? Now the N_2 partial pressure is greater than the partial pressure in equilibrium with a Ti/GaN contact that is fully reacted in a closed system. Hence, there is a thermodynamic driving force for the contact to incorporate nitrogen from the gas phase in order to equilibrate with its environment, and the annealing environment will nitride the contact. This is, in fact, exactly what we observe experimentally.

Fig. 3a shows an X-ray photoelectron spectroscopy (XPS) depth profile of a Ti/n-GaN film annealed at 700 °C in N_2 for 3 min, which reveals that nitrogen is present with an atomic concentration of approximately 50 % throughout the Ti layer and indicates the

presence of TiN. A small amount of Ga was detected at the surface of the nitrided Ti layer, indicating that some reaction did occur between the Ti and GaN. After the Ti layer was completely nitrided (partially from the GaN but primarily from N_2 gas), there was no evidence of further reaction with GaN upon longer term annealing. (These depth profiles of Ti contacts annealed in N_2 are somewhat different from what we previously reported for similar contacts that were annealed in sealed quartz tubes that had been backfilled with N_2 [10]. The N_2 pressure in the quartz tubes was actually much less than the 1 atm originally estimated and, therefore, the Ti layer was not completely nitrided.)

In contrast, XPS depth profiling of a sample that was annealed for even 25 min at 700 °C in Ar reveals that much of the Ti still remains unreacted, as shown in Fig. 3b. There is also evidence for greater consumption of GaN during annealing, as much more Ga is present in the reacted contact. Hence, these experiments point to the dramatic influence of the choice of annealing gas on the interfacial reactions in the contacts. The contacts annealed in N_2 also highlight the strong thermodynamic driving force for the formation of the stable TiN phase, which can not form as rapidly when contacts are annealed in Ar since the reaction between the Ti and GaN is slower than the reaction between Ti and N_2 gas. Based on ohmic contact measurements to be described later in this report, the annealing environment also plays an important role in the electrical characteristics of Ti/n-GaN contacts annealed at 700 °C. Consistent with the strong driving force for the formation of TiN (and ZrN), both the thermal and morphological stability of TiN-based and ZrN-based contacts are also outstanding, as will also be described in greater detail in the section on ohmic contacts to n-GaN.

In contrast to the early transition metals, a different type of behavior was expected for some of the middle transition metals. For example, Re and W were expected to provide stable thermally stable elemental contacts to GaN. In one case (Re), experimental evidence indicates that the contact metal does provide the excellent thermal stability predicted based on thermodynamics of the system. We annealed Re/GaN contacts for as long as 12 h at 600 °C and saw no evidence for reaction between the metal and semiconductor using x-ray diffraction. We also examined a contact annealed at 600 °C for 10 min using

high resolution transmission electron microscopy and found not only an intimate but an epitaxial contact, again with no evidence of reaction. This evidence is discussed together with findings from electrical characterization of Re/n-GaN contacts in the section on Schottky barrier contacts to n-GaN. In the other case (W), there is limited reaction between the metal and GaN at 600 °C concurrent with a clear change in the electrical properties of annealed W/n-GaN ohmic contacts, as reported by Cole *et al.* [11]. Apparently, predicted thermochemical data for the tungsten nitrides [12] underestimated the stability of the W_2N phase, which does in fact form upon annealing W/GaN contacts at 600 °C. Thus, W is not in thermodynamic equilibrium with GaN at 600 °C.

A very different nature of the contact metallurgy again was expected for the late transition metals and was in fact observed for Ni [13]. Nickel films 50 nm thick were deposited on GaN and annealed at temperatures between 400 °C and 900 °C in N_2, Ar, and forming gas before they were analyzed using glancing angle x-ray diffraction and Auger depth profiling. The first indication of an interfacial reaction was found after an anneal at 600 °C for 1 hour, after which Ga was observed to be dissolved in the face-centered cubic Ni film. The extent of dissolution increased with continued annealing. After annealing at 750 °C for 1 h in either N_2 or Ar, greater intermixing occurred. The reaction product was either Ni_3Ga or face-centered cubic Ni with dissolved Ga. Annealing at 900 °C for 10 min resulted in the formation of the B2 phase NiGa. It was clear from Auger depth profiles that the reacted film contained significantly more Ga than N and that N_2 gas was released to the annealing environment, even when the samples were annealed in N_2 gas at 1 atm. Thus, a trend of increasing Ga content in the reacted films was observed with increasing temperature. The observed reactions are consistent with the thermodynamics of the Ni-Ga-N system.

Interestingly, the interfacial reactions in Ni (500 Å)/GaN contacts are observed to occur along with balling up of the contact as the total interfacial energies are minimized [14]. Hence, the reaction between Ni and GaN is laterally non-uniform, and spiking of the contact into the underlying GaN has been observed in our laboratory. For these experiments, the contacts were chemically etched away after annealing, and atomic force mi-

croscopy (AFM) was performed on the newly-exposed GaN surface [14]. Examination of a sample that had been annealed in N_2 gas at 800 °C for 1 min revealed pits on the GaN surface as deep as 800 Å, suggesting that the contact metallization may have penetrated this deeply into the GaN. Because shallow ohmic contacts are required for many light emitting diode and laser structures, annealing Ni-based contacts at such high temperatures would not likely result in adequate contact uniformity and could even cause device failure with penetration of the contact metallization all the way through the underlying GaN layer.

3. Ohmic Contacts to n-Type GaN

Significant progress was made toward understanding the cause of the low contact resistivity of the most commonly used ohmic contacts to n-type GaN: Al/Ti/n-GaN and related Al-based contacts. In some cases, Al/Ti/n-GaN contacts become ohmic when TiN forms at the interface between the contact and GaN [15], presumably creating nitrogen vacancies and an increased donor concentration in the GaN near the contact/GaN interface, which promotes tunneling of carriers. However, studies conducted at The Pennsylvania State University reveal that another mechanism is actually responsible for the low observed contact resistivity under a variety of processing conditions.

GaN epilayers ($n = 7 \times 10^{17}$ cm^{-3}) obtained from Emcore Corporation were patterned and etched in dilute HCl, and both Al(115 nm)/Ti(35 nm)/n-GaN and Al(125 nm)/Pd(25 nm)/n-GaN contacts were deposited by sputter deposition. For Al/Ti/n-GaN, a contact resistivity of 4×10^{-6} $\Omega \cdot cm^2$ was obtained after annealing at 600 °C for 15 s in N_2 gas; for Al/Pd/n-GaN, a contact resistivity of 6×10^{-5} $\Omega \cdot cm^2$ was obtained after annealing at 600 °C for 30 s, similar to a report by Ping *et al.* [16]. The formation of TiN clearly does not occur in the Al/Pd/n-GaN contacts, nor would a palladium nitride form since the Pd-N bond is too weak. The similarity between the Al/Ti/n-GaN and Al/Pd/n-GaN contacts suggests that there is another reason why the Al-based contacts become ohmic upon annealing.

Interestingly, Auger depth profiles of a series of contacts annealed under a variety of conditions revealed that a low contact resistivity is obtained only after the Ti or Pd and the Al have intermixed, with the Al diffusing all the way to the contact/GaN interface. Even more importantly, direct evidence for the formation of a thin (2-3 nm) interfacial AlN layer between the contact and GaN in both ohmic contacts has been obtained at The Pennsylvania State University using two complementary techniques: high resolution transmission electron microscopy and high resolution energy dispersive spectroscopy.

Due to the wide band gap of AlN, we did not expect that its formation would improve the characteristics of the ohmic contacts. However, the AlN layer is thin enough for carriers to tunnel through it, and its presence could adjust the band line-up between the contact and GaN in such a way as to lower the potential barrier. A similar mechanism has been proposed for TiN ohmic contacts to n-type 6H SiC in which a thin amorphous layer of the insulator silicon nitride was detected at the TiN/SiC interface [17]. It is also possible that the formation of N vacancies in the GaN beneath the AlN could occur, also contributing to a decreased contact resistivity. Finally, a piezoelectric doping effect might be occurring.

At The Pennsylvania State University, the long term thermal stability of the Al/Ti/n-GaN ohmic contact has also been assessed and compared with a novel Al(35 nm)/Ta(115 nm)/n-GaN contact. The Al/Ta/n-GaN contact exhibited better mechanical integrity than did the Al/Ti/n-GaN contact [18]. Although repatterning with a conductive layer was necessary to minimize the influence of a high tantalum aluminide sheet resistance, the Al/Ta/n-GaN contacts annealed at 600 °C for 15 s exhibited a contact resistivity of 5×10^{-6} $\Omega \cdot cm^2$, comparable to that observed for Al/Ti/n-GaN contacts annealed under similar conditions. Annealed Al/Ti/n-GaN and Al/Ta/n-GaN ohmic contacts were further subjected to long term heat treatments in evacuated quartz tubes. Aging at 300 °C for 15 days or 400 °C for 9 days resulted in no measurable change in the contact resistivity, while aging for 5 days at 600 °C caused an increase in the apparent contact resistivities to 8×10^{-4} $\Omega \cdot cm^2$ and 3×10^{-3} $\Omega \cdot cm^2$ for Al/Ti/n-GaN and Al/Ta/n-GaN, respectively. By performing electrical characterization of samples repatterned with a conductive overlayer,

we discovered that the greatest contribution to the degradation of the contacts was due to an increase in the sheet resistance of the metal layer itself; the true interfacial resistance between the contact and GaN itself did not increase greatly.

An explanation for the observed electrical characteristics can be found from the observation that Al-based ohmic contacts Al/Ti/n-GaN and Al/Ta/n-GaN exhibit very good stability against continued reaction between the metal and semiconductor at 600 °C but less impressive resistance against agglomeration. A thin nitride layer (AlN in contacts examined at Penn State) is present at the contact/GaN interface, and this thin nitride layer appears to act as a diffusion barrier between the contact metallization and GaN. Thus, a very shallow reaction between the contact and underlying GaN is observed after annealing at 600 °C for 15 s. Even upon aging at this temperature for 5 days, the contact/GaN interface remains planar with minimal evidence of reaction, as confirmed by cross-sectional transmission electron microscopy. On the other hand, long-term aging of the contacts did result in considerable phase segregation and island formation in both Al/Ti/n-GaN and Al/Ta/n-GaN contacts, since 600 °C is near the melting point of the Al phase (660 °C) present in these contacts. The morphological degradation of the metal film is largely responsible for a dramatic increase in the sheet resistance of the metal and the apparent increase in the contact resistivity. (An apparent increase in the contact resistivity is an artifact of a high sheet resistance of the metal film when contact resistivity is determined by the transmission line method. Actually, the contact resistivity is an interfacial property and in this case does not increase greatly upon aging, as confirmed by re-patterning the contacts with a conductive overlayer and again measuring the contact resistivity.)

Ohmic contacts to n-GaN examined in our laboratory that provided improved morphological stability compared to the Al-rich contacts described above include TiN/Ti/n-GaN and ZrN/Zr/n-GaN. (Preliminary evidence indicates that more Ti-rich Al/Ti/n-GaN contacts are also more stable morphologically than the Al-rich Al/Ti/n-GaN in common use today.) The following paragraphs highlight our work leading to the development of stable, low resistance TiN/Ti/n-GaN and ZrN/Zr/n-GaN contacts.

As described above, metallurgical considerations suggest that TiN and ZrN contacts to n-GaN should offer excellent thermal and morphological stability as ohmic contacts to n-GaN. However, TiN (200 nm)/n-GaN contacts examined in our laboratory never achieved specific contact resistances as low as those of annealed Ti(150 nm)/n-GaN contacts in which TiN formed [7]. The TiN/n-GaN contacts reached an ultimate specific contact resistance of 4 x 10^{-5} $\Omega \cdot cm^2$ after they were annealed at 800 °C for 1 min. Although Ti/n-GaN contacts were rectifying as-deposited, when annealed in N_2 gas, they became ohmic with a specific contact resistance of 1×10^{-3} $\Omega \cdot cm^2$ after an anneal at 700 °C for 1 min in N_2, and annealing in N_2 for 1 min at either 800 °C or 900 °C resulted in a specific contact resistance of 4×10^{-6} $\Omega \cdot cm^2$. (Contacts annealed in Ar required higher annealing temperatures or longer annealing times to become ohmic. They remained rectifying when annealed in Ar at 700 °C for 1 min and became ohmic after 1 min at 800 °C with a specific contact resistance of 6×10^{-6} $\Omega \cdot cm^2$. Only after a 1 min anneal at 900 °C did the contacts annealed in Ar reach a specific contact resistance of 4×10^{-6} $\Omega \cdot cm^2$. The more severe annealing conditions were required because the Ar annealing environment could not contribute nitrogen to speed the formation of TiN, which is necessary for the formation of the ohmic contact [7].) All of these contacts retained smooth surfaces after annealing. Unlike the directly deposited TiN contacts we studied, however, all of the reacted Ti contacts required repatterning with a conductive overlayer to lower the sheet resistance of the metal to avoid measuring an artificially high specific contact resistance by the TLM method.

The differences in the electrical characteristics of the contacts were correlated with differences in the contact metallurgy [7]. Titanium nitride was found in contact with the n-GaN in all of the ohmic contacts. Reaction between the contact and GaN, however, was necessary to achieve the lowest specific contact resistance. Measurements of the specific contact resistance as a function of temperature revealed that interfacial reaction with the semiconductor promoted a different transport mechanism in the reacted Ti contacts than in the directly deposited TiN contacts. From 77–300 K, the specific contact resistance of the directly deposited TiN/n-GaN contacts (n = 7 x 10^{17} cm^{-3}) varied with temperature, indicating a thermionic emission component of the current, while the specific contact re-

sistance of the low resistance reacted contacts was independent of temperature. As first suggested by Lin *et al.* [19], N vacancies may form in the GaN under the reacted Ti contacts, causing heavy doping and a thinner potential barrier in the semiconductor that allows current transport by field emission. (It is important to note, however, that the contacts annealed in Ar may undergo extensive reaction with GaN before both TiN forms and ohmic contact properties result. In this case, reaction between Ti and GaN could first cause stoichiometric decomposition of GaN rather than the formation of N vacancies.)

Because of the need for interfacial reaction between the Ti and GaN to result in the lowest contact resistivity and because of the thermal stability of the directly deposited TiN contacts, Kaminska *et al.* [20] and our group [7] have both investigated TiN (200 nm)/Ti (5 nm)/n-GaN contacts that are promising for applications in which the thermal stability is important. We obtained a specific contact resistance of 6×10^{-6} $\Omega\bullet cm^2$ for the TiN/Ti/n-GaN contacts annealed in Ar for 1 min at 800 °C. One advantage of the TiN/Ti/n-GaN contact structure is that the amount of reaction with GaN can be controlled by the Ti layer thickness. Furthermore, unlike our own and Wu's Ti-only contacts [8], these contacts did not require a separate overlayer to lower the sheet resistance of the metal film. Furthermore, the contacts exhibited no degradation after they were annealed at 600 °C for 5 days in evacuated quartz tubes. Even more severe aging conditions were tested for ZrN (200 nm)/Zr (5 nm)/n-GaN ohmic contacts. These contacts exhibited excellent thermal stability during aging in evacuated quartz tubes at 600 °C for 1000 h. When fabricated on the same piece of n-GaN as the TiN/Ti/n-GaN contacts, however, they exhibited a higher ultimate specific contact resistance (2×10^{-5} $\Omega\bullet cm^2$) and required more severe annealing conditions, a finding that was linked to slower reaction kinetics between Zr and GaN compared to Ti and GaN [6].

The discussion presented here and results from the literature demonstrate that low resistance ohmic contacts to n-GaN can now readily be fabricated, and solutions are available for situations where thermal stability is critical or where shallow contacts may be required. As it becomes necessary to fabricate ohmic contacts to n-AlGaN, however, the problem of ohmic contacts to the n-type semiconductor will become more challenging.

4. Schottky Barriers to n-Type GaN

Schottky barrier contacts to n-GaN are of interest for ultraviolet detectors (although not for solar blind detectors) and for high frequency and high power nitride electronic devices. Fundamental information about Schottky barrier contacts is also of interest when designing ohmic contacts to a semiconductor. For n-GaN, barrier heights of 1 eV and greater have been reported for Au, Pd, Pt, and Ni Schottky contacts to n-GaN [21]. However, metals like Au, Pd, Pt, and Ni form stable metal gallides and are prone to reaction with GaN upon prolonged exposure to high temperatures.

Metal-III-V phase diagrams and studies of reactions between metal thin films and GaN can be used to identify metals, binary, and ternary phases that are in thermodynamic equilibrium with the semiconductor. When such a phase results in a contact that has desirable electrical properties, it may be directly deposited to create a uniform, thermally stable, non-reactive contact. We have observed in our study of interfacial reactions between Ni thin films and GaN that the Ga content in the reacted films increased with increasing annealing temperature and that N_2 gas was simultaneously released to the annealing environment. The Ga content increased from approximately 15 at % at 600 °C to 25 at % at 750 °C following long-term annealing. A directly deposited Ni-15 at % Ga contact would therefore be thermodynamically stable on GaN at temperatures at least as high as 600 °C. Another example of a contact in thermodynamic equilibrium with GaN at 600 °C would be a Re contact. (In fact, been recently confirmed experimentally [22] that Re contacts are metallurgically stable on GaN for annealing conditions as severe as 30 min at 800 °C.) The high work function of Re [3], combined with its thermal stability, makes it an attractive candidate for a thermally stable Schottky contact on n-GaN.

We therefore examined the electrical characteristics and thermal stability of Ni/Ga/Ni (15 nm/15 nm/26.7 nm) and 70 nm Re contacts. Current-voltage measurements were performed at 150 °C in air, and capacitance-voltage measurements were performed at room temperature as a function of annealing temperature for 10 min anneals in N_2 gas. Elemental Ni Schottky contacts were also investigated for comparison.

The barrier height of the Ni/Ga/Ni Schottky diodes increased to a maximum upon annealing at 600 °C, with a barrier height of 0.75 and ideality factor of 1.07 obtained by current-voltage (I-V) measurements. Using capacitance-voltage (C-V) measurements, a barrier height of 0.87 eV was obtained. (Consistent with previous reports by other researchers [23, 24], initial improvement in the characteristics of Schottky barrier contacts to n-GaN was observed.) For the elemental Ni diodes, the barrier height increased to a maximum of 0.89 eV upon annealing to 500 °C, as determined using the I-V technique. It can be seen that the maximum barrier height is higher for the Ni contact as compared to the Ni/Ga/Ni contact. In the absence of complete Fermi level pinning, the barrier height for a metal on an n-type semiconductor is expected to increase with metal work function. Since the work function of Ni is higher than that for Ga, one can assume to a first approximation that the work function of a Ni/Ga/Ni contact decreases with increasing Ga content. This would explain the higher barrier height for the Ni only contact. The Ni diodes, however, start degrading after annealing at 550-600 °C, while the Ni/Ga/Ni diodes were stable upon further annealing to 700 °C. The degradation of the Ni diodes is most likely due to Ga dissolution in the contact. As expected, the Ni/Ga/Ni diodes are more stable due to the inert nature of the interface between the Ni/Ga/Ni contact and GaN at the temperatures used in this study.

The barrier height of the Re diodes increased upon annealing at 400 °C. After the 500 °C anneal, the barrier height obtained by I-V measurements was 0.82 eV with an ideality factor of 1.1, while the barrier height by the C-V technique was 1.06 eV. No further change in the barrier height occurred upon annealing from 500–700 °C. Upon continued annealing for 1 min at 900 °C, the barrier height decreased; however, the diodes remained well-behaved. These thermally stable contact materials were also found to be thermally stable contacts to p-GaN.

5. Ohmic Contacts to p-Type GaN

Although considerable progress has been made toward increasing the level of p-type doping in GaN, achieving low resistivity ohmic contacts to p-GaN has been challenging.

Limiting factors have included not only the difficulties in doping, but also the higher carrier effective mass compared to n-GaN and possibly high Schottky barrier heights, although very few reliable measurements of barrier heights to p-GaN have been performed. Because of the difficulties in forming ohmic contacts to p-GaN, non-linear I-V characteristics are frequently obtained at room temperature. Currently, Ni/Au is commonly used as an ohmic contact to p-GaN [25, 26]. Other contact schemes include high work function metals such as Ni, Au, Pt, and Pd [27–29], sometimes with an additional layer of Cr [30–32]. The contacts are usually annealed at temperatures between 400 °C and 750 °C, and contact resistivities near 10^{-2} Ω•cm^2 are common, with a value as low as 1.2×10^{-4} Ω•cm^2 reported for Cr/Au contacts to MBE-grown p$^+$-GaN [32]. Studies often show contact resistivities clustered around a small range of values when contacts are fabricated on the same p-GaN epilayer [27, 28].

We tested a wide variety of metallizations annealed in N_2 gas for times from 10 s to 10 min at temperatures from 400–800 °C. We selected these contacts for a variety of reasons. We examined single metal and bimetallic contacts of high work function metals, since for n-GaN it is possible to exercise some control over the Schottky barrier height through the metal work function. Metals with high work functions would therefore be expected to yield lower barrier heights to p-GaN and be more suitable for contacts to p-GaN. The contacts we tested included Au/Ni/p-GaN, Pt/Ni/p-GaN, Au/Co/p-GaN, Au/Pd/p-GaN, Au/p-GaN, Pd/p-GaN, Ni/p-GaN, Pt/p-GaN, and Re/p-GaN. Although not a high work function metal, elemental Cr was also tested. Most of the contacts were deposited by sputter deposition. In the case of Ni, however, a comparison was made between sputtered, electron beam evaporated, and thermally evaporated contacts. For Pt, a comparison between electrodeposition and sputter deposition was performed. Some contacts were selected for their anticipated thermal stability so that we could anneal the contacts at higher temperatures than we could contacts such as Au/Ni/p-GaN, without the complication of a degraded contact morphology or extensive decomposition of the semiconductor through metallurgical reaction. It was our hope that higher annealing temperatures might result in lower contact resistivities or even improved activation or reactivation of Mg acceptors. The contacts we tested in this category included PtSi/p-GaN,

Re/p-GaN, and Ni/Ga/Ni/p-GaN. Although the anticipated thermal stability was observed experimentally, none of these contacts exhibited electrical characteristics even as good as standard Au/Ni/p-GaN contacts. Still other contacts were selected for their potential to form a narrower gap intermediate semiconducting layer between the metal and semiconductor, since this approach has been used to advantage in contacts to conventional III-V semiconductors. In this case, we tested PdIn and TiSb in attempts to form intermediate layers of InN and GaSb, respectively. We also tested Al/Pd/p-GaN contacts to examine the influence of a very thin interfacial layer of AlN between the metal and semiconductor, as this situation was found to produce low resistance contacts to n-GaN. Finally, we explored the role of the surface preparation prior to metallization and the influence of the metal deposition method on the electrical characteristics of contacts to p-GaN.

Our best contacts to p-GaN were clearly sputtered Pt/Ni/p-GaN and electrodeposited Pt/p-GaN contacts [33]. As can be seen in Fig. 4, these contacts provided much more linear I-V curves than did sputtered Au/Ni/p-GaN or sputtered Pt/p-GaN contacts, while all of the other contacts listed in the above paragraph presented electrical characteristics comparable to or worse than the Au/Ni/p-GaN contact. Although the I-V curves are not perfectly linear, "effective" contact resistivities were extracted from measurements performed at a constant current, in this case 10 mA. Comparisons between contacts were repeated several times on the same wafer of p-GaN supplied by Emcore ($p = 4.6 \times 10^{17}$ cm^{-3}). Averages of the effective contact resistivities for at least three separate deposition runs of the sputtered Pt/Ni/p-GaN ($1.5–1.8 \times 10^{-2}$ $\Omega \cdot cm^2$ depending on layer thicknesses), electrodeposited Pt contacts (1.5×10^{-2} $\Omega \cdot cm^2$), and several other contacts are provided in Table 1 along with the final annealing condition for which these values are reported. In all of these experiments, cumulative anneals of 5 min at 400 °C, 1 min at 500 °C, 1 min at 600 °C, and 1 min at 700 °C were used, and an "effective" contact resistivity was measured after each stage of annealing. More recent studies suggest that subjecting samples directly to the optimal annealing temperature without the intermediate annealing steps does not give significantly different results.

The values for Pt/Ni/p-GaN and electrodeposited Pt/p-GaN can be compared to average effective contact resistivities from 3–5 x 10^{-2} Ω•cm^2 (or in a few cases even higher values) for all of the other contacts studied. Earlier results for pulsed electrodeposition of Pt (accomplished by tapping wires together for the pulses) actually provided even lower contact resistivities (in the 10^{-3} Ω•cm^2 range); however, we have not yet been able to reproduce these results using a signal generator. It is also important to note that the same relative ranking of the contacts of greatest interest (electrodeposited Pt, sputtered Pt, Ni/Pt, and Ni/Au) was obtained on p-GaN obtained from Cree research, although the p-GaN layer was part of an LED structure, and no attempt to extract a contact resistivity from these samples was made.

We have formulated a hypothesis to explain the superiority of the electrodeposited Pt and sputtered Pt/Ni/p-GaN contacts over the other contacts we studied. Earlier studies have indicated that a contamination or oxide layer exists on GaN layers exposed to air [34]. The presence of such a layer has been shown for other contacts to hinder current transport [35], and should such a layer be removed more effectively in the plating bath, a lower contact resistivity might be expected for the electrodeposited contacts than for sputtered Pt contacts deposited on GaN surfaces that were exposed to air before they were loaded into a vacuum system for metal deposition. Similarly for the annealed Pt/Ni/p-GaN contacts, an intimate interface between a high work function solid solution containing Pt and the GaN could also be created. Supporting this hypothesis is the earlier study by Ishikawa *et al.* [36] that demonstrates by high resolution transmission electron microscopy that a short term anneal at 400 °C is sufficient to allow Ni to penetrate an observable contamination layer on GaN, resulting in an intimate contact. Furthermore, our Auger depth profiles show that the lowest contact resistivity is obtained for Pt/Ni/p-GaN only after interdiffusion of Ni and Pt to form a solid solution in contact with GaN. Thus, the higher work function of Pt (5.65 eV [37]) in the Ni-Pt solution, as compared to that of Ni (5.15 eV [37]) and Au (5.1 eV [37]), could be responsible for the lower resistivity of the Pt/Ni/p-GaN contacts, while Ni could be beneficial because it can readily penetrate the contamination layer on GaN, creating a more intimate contact. This hypothesis is further supported by the observation that reducing the Ni layer thickness from 50 nm to

10 nm further improves the contact, since the Ni-Pt solution that ultimately forms is richer in Pt when the Ni layer is thinner.

Our recent findings about the role of surface preparation and the need for forming an intimate contact, as well as our findings about the advantage of the Ni and Pt metal combination, are mirrored by a couple of very recent reports in the literature. Kim *et al.* recently compared Au/Pd/p-GaN contacts prepared without any chemical treatment of the p-GaN surface to contacts prepared on p-GaN surfaces subjected to boiling aqua regia (HNO_3:HCl, 1:3) prior to metallization [38]. A dramatic improvement in the contact resistivity (by two orders of magnitude) was obtained. Indeed, we have in our own laboratory observed that for sputtered Pt contacts, first subjecting the p-GaN surface to a variety of hot acids and bases (boiling aqua regia, KOH at 95 °C, boiling NH_4OH) prior to metallization results in improved contact performance compared to when the p-GaN is subjected to acids at room temperature (HCl or buffered HF). However, in none of our Pt/p-GaN contacts do the effective contact resistivities approach those obtained for our electrodeposited Pt contacts. Jang *et al.* have also recently reported a promising Au/Pt/Ni/p-GaN contact [39].

Although encouraging progress has been made, continued improvement in the performance of ohmic contacts to p-GaN is still needed. In fact, the problem will be even more challenging should it become necessary to contact p-AlGaN. Improvements have been demonstrated in this work through the use of electrochemical means to deposit the contacts (an approach that has not yet been fully exploited) and through the choice of favorable metallizations deposited by conventional physical vapor deposition. Also in need of further investigation is the approach very recently described by Murakami and Koide for processing ohmic contacts in O_2 (for late transition metal contacts) or vacuum (for early transition metal contacts [40]). Both of these techniques are believed to improve the activation of Mg acceptors in the p-GaN, in some cases providing record low contact resistivities. Unfortunately, oxidation and long term stability of these particular contacts (even at moderate temperatures) remain serious problems.

6. References

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7. Tables and Figures

Table 1. Comparison of effective contact resistivities at a measurement current of 10 mA for contacts to p-GaN.

Metallization Scheme	**Optimal Annealing Schedule**	**Effective Contact Resistivity x 10^{-2} $\Omega \cdot cm^2$**
Pt (70 nm) Electrodeposited	600 °C 1 min	1.5 ± 0.2
Ni(50 nm)/Pt(100 nm) sputtered	600 °C 1 min	1.8 ± 0.4
Ni(10 nm)/Pt(100 nm) sputtered	600 °C 1 min	1.5 ± 0.3
Ni(50 nm)/Au(100 nm) sputtered	400 °C 5 min	3.3 ± 1.3
Pt(50 nm) sputtered	700 °C 1 min	4.8 ± 1.7

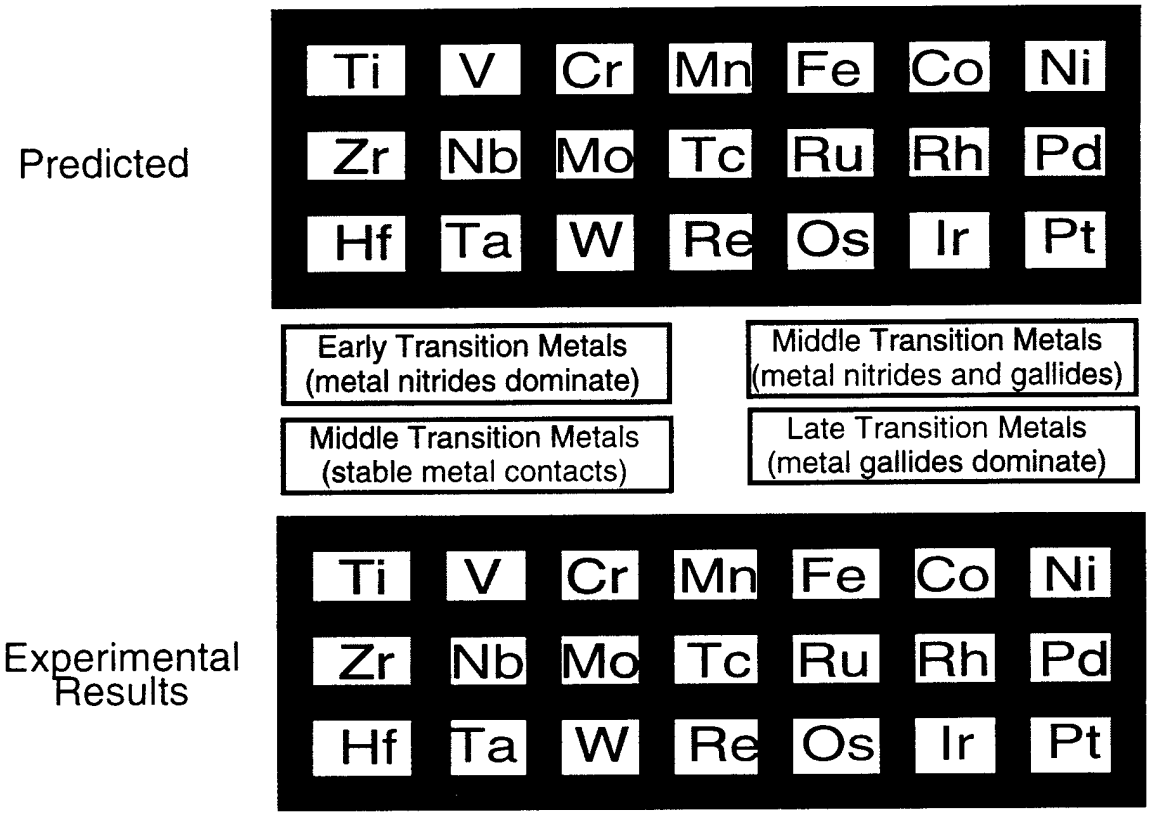

Figure 1. Predicted (top) and experimentally determined (bottom) characteristic features of the metal-Ga-N phase equilibria.

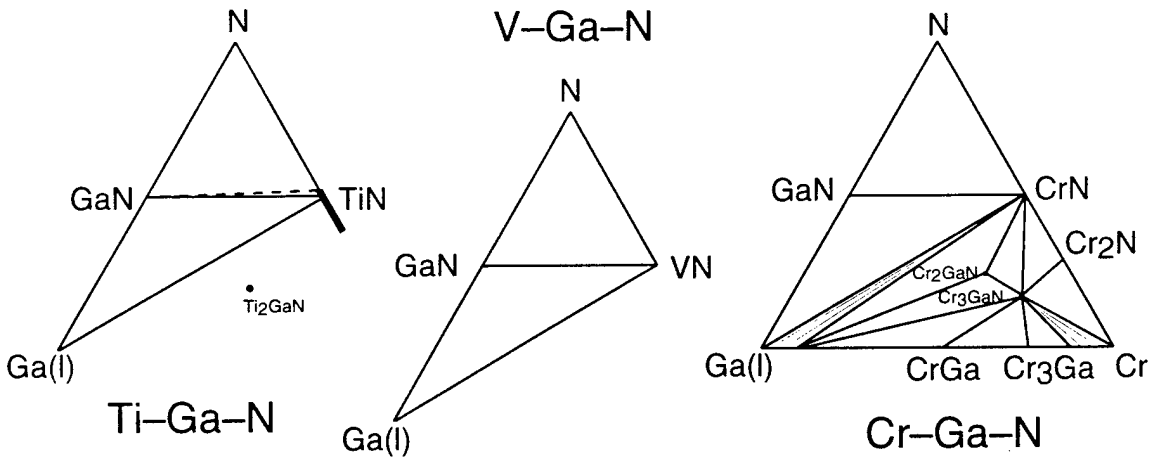

Figure 2. Portions of isothermal sections of the Ti-Ga-N, V-Ga-N, and Cr-Ga-N phase diagrams experimentally determined at 800 °C.

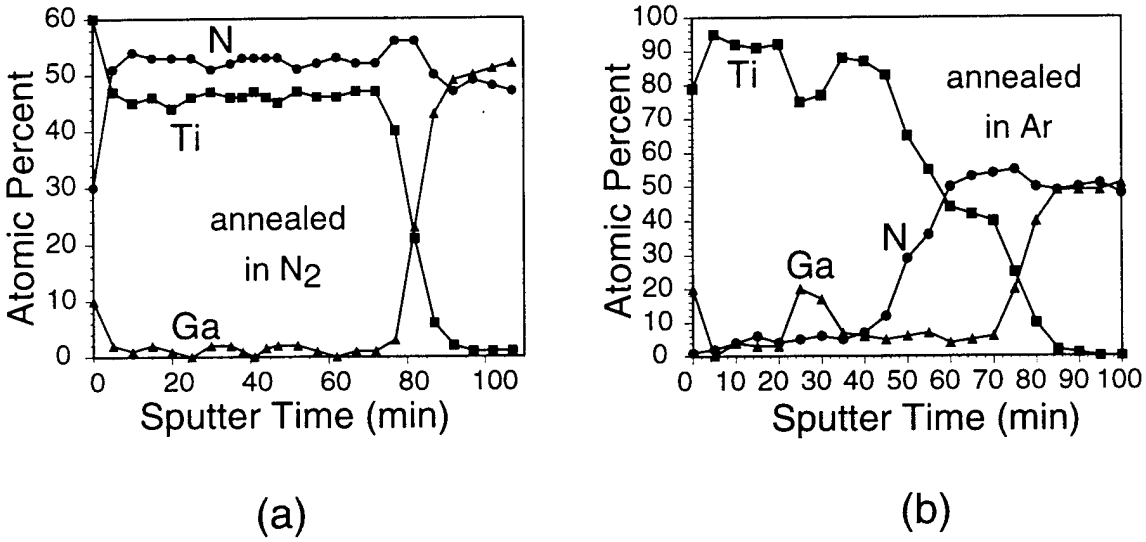

Figure 3. XPS depth profiles of Ti/GaN contacts annealed at 700 °C in (a) N_2 for 3 min and (b) Ar for 25 min.

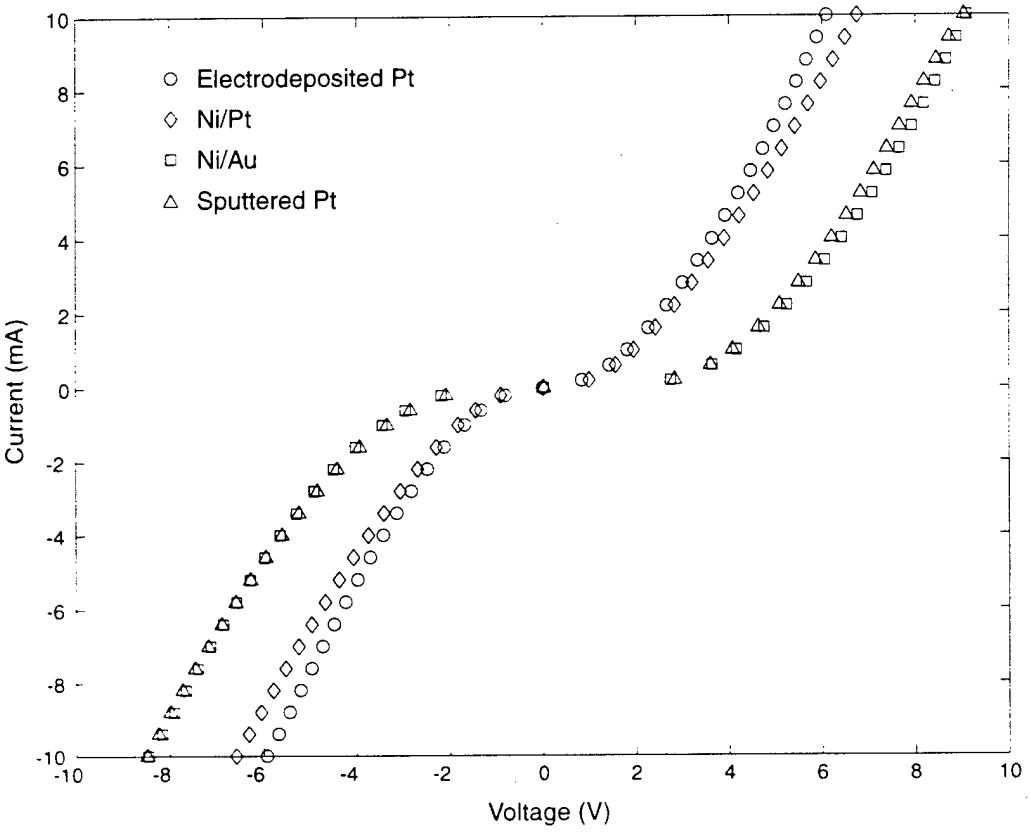

Figure 4. I-V curves for sputtered Pt, Ni/Pt, and Ni/Au and electrodeposited Pt contacts. The gap spacing in the circular TLM pattern was 50 μm.

8. Publications Resulting from Award

1. S. E. Mohney, "Ohmic Contacts to GaN and the Group III Nitride Semiconductor Alloys," in Properties of Gallium Nitride and Related Compounds, ed. J. H. Edgar, INSPEC, London, in press.

2. S. E. Mohney, "Schottky Barrier Contacts to GaN," in Properties of Gallium Nitride and Related Compounds, ed. J. H. Edgar, INSPEC, London, in press.

3. S. D. Wolter, B. P. Luther, and S. E. Mohney, "Thermally Stable ZrN/Zr/n-GaN Ohmic Contacts," Electrochemical and Solid-State Letters, in press.

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Contacts to GaN," High Temperature Materials Chemistry, ed. K. E. Spear (The Electrochemical Society Proceedings 97-39, 1997), 101.

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9. Personnel Associated with the Project

Principal Investigator (12%)	Suzanne Mohney	9/95–9/98
Postdoctoral Assistants	Hari Venugopalan	8/96–9/98
Graduate Students	Brian Luther	9/95–11/97
	Xin Lin	9/95–4/96
	John DeLucca	6/97–8/98 (part-time)
Undergraduate Students	David MacMahon	6/96–8/96
	Heather Miller	9/96–12/97
	Nina Folino	9/96–12/97
	Keith Whitmire	1/97–5/97

Two students prepared dissertations based on work they performed on this project. Brian Luther earned a Ph.D. in Electrical Engineering from The Pennsylvania State University in December, 1997. Xin Lin earned her M.S. degree in Materials Science in December, 1997. The main conclusions from their theses are included in the technical discussion in this report. The titles and abstracts of these theses are also included on the following pages. The complete theses may be obtained from The Pennsylvania State University (Library Phone: (814) 865-2112).

10. Thesis Abstracts

Estimation of Transition Metal-Ga-N Ternary Phase Diagrams for the Development of Electrical Contacts to GaN

M.S. Thesis in Materials Science
Xin Lin
December, 1997

Abstract

Gallium nitride has been used in the fabrication of electronic and optoelectronic devices. Forming low resistivity ohmic contacts and low leakage Schottky barriers to GaN that exhibit good thermal stability is critical to the development of GaN based devices. In order to provide guidance for further experimental study on electrical contacts to GaN, transition metal-Ga-N ternary phase diagrams at room temperature (25 °C) and high temperature (600 °C) were estimated in this thesis. Although insufficient thermodynamic data are available to make precise predictions of the phase equilibria, distinct trends have been revealed for the features of the metal-Ga-N systems according to the position of the metal in the periodic table. MN phases are predicted to be in equilibrium with GaN for early transition metal-Ga-N systems. Some middle transition metals, such as Re, are thermally stable elemental contacts to GaN. For the late transition metals, metal gallides are predicted to be stable with GaN, with the composition of the stable metal gallide depending upon the partial pressure of N_2 gas.

Titanium and Aluminum-Based Ohmic Contacts to n-Type Gallium Nitride

Ph.D. Thesis in Electrical Engineering
Brian P. Luther
December, 1997

Abstract

A systematic investigation of ohmic contacts to n-type GaN was undertaken in order to better understand the mechanisms by which these contacts form. Specific contact resistance measurements, x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) depth profiles, and high resolution transmission electron microscopy (HRTEM) were used to investigate the annealing conditions, electrical properties, and metallurgical properties of Al- and Ti-containing contacts to n-type GaN.

A study of Ti/Al contacts annealed between 400 and 600 °C revealed that low resistance ohmic contacts only formed after the Al and Ti layers had intermixed and Al had diffused to the metal/GaN interface. A thin layer of AlN was then observed by HRTEM at the metal/GaN interface of both Ti/Al and Pd/Al ohmic contacts. Based on these observations, it is proposed that Al-containing contacts to n-type GaN become ohmic due to the formation of an AlN layer at the interface through which electrons can tunnel, and which alters the potential barrier in the GaN. Ta/Al contacts were fabricated for the first time and behaved similarly to Ti/Al and Pd/Al contacts, becoming ohmic only after Ta and Al layers intermixed significantly.

Ti-containing contacts were investigated by annealing in N_2 and Ar atmospheres at temperatures from 400 to 900 °C. It was concluded that the primary reason for ohmic contact formation in Ti and TiN contacts was TiN in contact with GaN. Ti contacts that reacted with GaN to form TiN reached lower contact resistivities than deposited TiN contacts that underwent similar annealing conditions.

The long term stability of ohmic contacts to n-type GaN was studied, revealing that Ti/Al and Ta/Al contact resistivities increase when aged at 500 °C and above due to the degradation of the metal contact layer. TiN contacts did not degrade when aged at 600 °C for 5 days, indicating that they may be a better ohmic contact for device applications where contact reliability at elevated temperatures is a concern.

Abstract

(repeated from Report Documentation Page)

The metallurgy and electrical performance of contacts to GaN were examined. Thermodynamic estimates coupled with experimental work revealed clear trends in the nature of the contact metallurgy depending upon the position of the metal in the periodic table. This information was then used to aid in the investigation and design of electrical contacts to GaN. Ohmic contacts to n-GaN, Schottky barriers to n-GaN, and ohmic contacts to p-GaN were fabricated and characterized. These studies resulted in an improved understanding of the mechanism of ohmic contact formation in Al/Ti/n-GaN contacts, along with the development of TiN/Ti/n-GaN and ZrN/Zr/n-GaN ohmic contacts with exceptional thermal stability at 600 °C and contact resistivities of 6×10^{-6} and 2×10^{-5} $\Omega \cdot cm^2$, respectively, for $n = 7 \times 10^{17}$ cm^{-3}. Also developed were Re/n-GaN Schottky barrier contacts that were stable upon annealing at 700 °C with current-voltage and capacitance-voltage barrier heights of 0.82 and 1.06 eV, respectively. For ohmic contacts to p-GaN, a large number of contacts were evaluated. A clear improvement over conventional Au/Ni/p-GaN contacts was provided by electrodeposited Pt/p-GaN and sputtered Pt/Ni/p-GaN contacts, which provided contact resistivities that were lower than Au/Ni/p-GaN contacts by more than a factor of two. An explanation for this improvement was formulated.